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(54) Title: **CATALYST FOR THE DEHYDROGENATION OF ETHYLBENZENE TO STYRENE**

(57) Abstract: The present invention relates to a catalyst for the dehydrogenation of ethylbenzene to styrene and to a process for the preparation thereof. The catalyst contains iron oxide, potassium oxide and calcium oxide, preferably also cerium oxide and molybdenum oxide, and is characterised by a magnesium content (expressed as MgO) lower than 0.001 %.

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Rec'd PGT/PTO 04 OCT 2004**CATALYST FOR THE DEHYDROGENATION OF ETHYLBENZENE
TO STYRENE****STATE OF THE ART**

The industrial production of styrene from ethylbenzene started in the Forties, but a large scale production started only in the Fifties, by means of a catalyst based on $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-K}_2\text{CO}_3$, calcined at very high temperature, usually higher than 900°C (US 2,461,147). Due to the high calcination temperature, this catalyst, known with the trade name Shell 105, was characterised by high mechanical strength, but had low selectivity to styrene. A dramatic selectivity improvement was achieved with catalysts based on $\text{Fe}_2\text{O}_3\text{-K}_2\text{CO}_3\text{-MoO}_3\text{-CeO}_2$ (US 3,904,552), which required a much lower calcination temperature (ca. 500°C). In order to confer mechanical strength to these catalysts it was necessary to add Portland cement, which contained other elements, whose characteristics were detrimental to the catalytic process. More recently (US 4,467,046), it has been found that the addition of a calcium compound (oxide or carbonate) to the formulation disclosed in US 3,904,552, allowed to avoid the addition of Portland cement and its negative effects. Nevertheless, the addition of calcium oxide and carbonate renders the catalysts relatively fragile.

DESCRIPTION OF THE INVENTION

It has now surprisingly been found that catalysts for the dehydrogenation of ethylbenzene to styrene which contain calcium oxide or carbonate are mechanically more resistant, more active and more selective when the magnesium content of the calcium oxide precursor and of the resulting catalyst is particularly low.

The present invention provides a catalyst containing iron oxide, potassium oxide and calcium oxide, preferably also cerium oxide and

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molybdenum oxide, characterised in that the magnesium content is lower than 0.001%. Preferably, the catalyst comprises (expressed as weight % of oxides): 50-95% iron oxide (Fe_2O_3), 5-20% potassium oxide, 0.2-14% calcium oxide, 0.5-20% cerium oxide and 0.2-8% molybdenum oxide. A more preferred composition comprises: 60-85% iron oxide (Fe_2O_3), 5-15% potassium oxide, 0.5-2% calcium oxide, 5-15% cerium oxide, 0.5-2% molybdenum oxide. A most preferred composition comprises: 75-80% iron oxide (Fe_2O_3), 8-12% potassium oxide, 0.7-1.4% calcium oxide, 8-12% cerium oxide, 0.7-1.4% molybdenum oxide.

10 The catalyst of the invention can be prepared from iron, calcium, potassium, cerium and molybdenum salts, hydroxides or variously hydrated oxides, easily available on the market, the magnesium content of said compounds being such that the final catalyst contains less than 0.001% by weight of magnesium (expressed as magnesium oxide).

15 A further object of the present invention is therefore a process for the preparation of the catalyst comprising the following steps:

- pre-mixing iron, calcium, potassium, cerium and molybdenum salts, hydroxides or variously hydrated oxides having a magnesium content such that the final catalyst contains less than 0.001% by weight of magnesium (expressed as magnesium oxide);
- 20 - adding a solution or a suspension of a binder-lubricating agent so as to obtain a paste;
- extruding a paste in cylindrical particles of diameter and length ranging from 2 to 6 mm;
- 25 - submitting said cylindrical particles to drying and calcination characterised in that calcination is carried out for a time range from 30 minutes to 10 hours, preferably from 1 to 4 hours, at a temperature ranging from 950 to 990°C, preferably from 960 to 980°C and more

preferably from 965 to 975°C.

Pre-mixing can be carried out by means of conventional techniques, such as dry or wet milling, e.g. in a ball mill or in another suitable apparatus and added with a proper amount of a solution or suspension of a binder-lubricating agent, such as stearic acid, carboxymethyl-cellulose, polyethylene glycol, glycerol, starch of various origin and similar compounds, so as to form a paste of the proper consistency, suitable for the extrusion in cylindrical particles. Before calcination, the extruded cylinders are dried at a temperature between 50 and 120°C, preferably between 60 and 100°C.

The catalyst of the invention can be conveniently used for the dehydrogenation of ethylbenzene to styrene by passing a flow of ethylbenzene and water vapour through a bed of catalyst particles, with a "steam/oil" (S/O) water/ethylbenzene weight ratio between 2.5 and 1.0, preferably lower than 2. It is well known that the lower the S/O ratio, the lower the energy consumption of the process, but the higher the risk of catalyst deactivation, due to deposition of carbonaceous compounds. A nitrogen flow is added to these two reactants, so as to give a volumetric dilution ratio (RD) of the gaseous flows (ethylbenzene + water)/(ethylbenzene + water + nitrogen) between 0.1 and 1, preferably between 0.4 and 0.6.

The present invention will be now illustrated in further detail by means of some examples.

EXAMPLES

Examples 1-5

A mixture of finely powdered iron oxide, cerium carbonate, calcium carbonate, potassium carbonate and potassium molybdate, in proper weight ratios, (said mixture containing less than 0.001% by weight of magnesium, expressed as magnesium oxide) has been dry milled for 4 hours in a corundum ball mill, so as to give a final catalyst with the following weight %

composition: Fe_2O_3 78, CeO_2 10, CaO 1, K_2O 10, MoO_3 1. A 5% by weight aqueous suspension of carboxymethyl-cellulose as binder-lubricating agent has been then added to the mixture so as to form a paste having a consistency suitable for extrusion through a die with holes 3 mm in diameter. The extrudates have been dried overnight at 80°C in an oven and divided in 5 portions. The latter have been calcined separately in flowing air, with a temperature ramp of $1^\circ\text{C}/\text{min}$, up to 900, 950, 970, 990 and 1000°C , respectively. The final calcination temperature has been maintained for 3 hours and then the samples have been allowed to cool down to room temperature. The cylindrical particles thus obtained (3 x 3 mm in size), have been subjected to the crushing strength essay, as described in the literature (see e.g. J.T. Richardson, "Principal of catalyst development", Plenum Press, New York 1989) and then crushed and sieved, and the 40-60 mesh fraction (samples IC1-90, IC1-95, IC1-97, IC1-99 and IC1-100) has been recovered.

Every sample has been tested by loading 1 g of catalyst in a continuous tubular laboratory reactor, made of Incoloy 800 alloy (internal diameter 9 mm, with an axial thermo well of 1.6 mm external diameter). A nitrogen flow has been then fed to the reactor and the temperature was raised by $3.17^\circ\text{C}/\text{min}$ up to 400°C , then by $1.75^\circ\text{C}/\text{min}$ up to 610°C , then maintained. The feeding of water and of ethylbenzene was started at 300°C and at 550°C , respectively. The space velocity (LHSV) was 0.7 cm^3 of ethylbenzene/(hour x cm^3 of catalyst bed), the S/O ratio was 2 and the RD ratio was 0.5.

The samples of reactor effluent for the determination of the activity and selectivity of the catalyst, have been collected by means of traps, cooled to 40°C by a cryostat. The conversion of ethylbenzene and the selectivity to styrene have been determined at 48 hours-on-stream, by gas-chromatographic analysis of the effluent samples collected in the traps. The results of the mechanical strength and catalytic activity assays are reported in table 1.

Example 6

A sample of catalyst, referred to as IC3-97a, consisting of: Fe₂O₃ 78%, CeO₂ 10%, CaO 1%, K₂O 10%, MoO₃ 1%, prepared by employing as CaO precursor a commercial calcium carbonate containing 0.5% by weight of magnesium carbonate, and operating as described in examples 1-5, has been calcined at 970°C and tested under the conditions described above. The results are reported in Table 1.

Example 7

A sample of catalyst, referred to as IC3-97b, consisting of: Fe₂O₃ 77%, CeO₂ 10%, CaO 1%, K₂O 10%, MoO₃ 1%, MgO 1%, has been calcined at 970°C and tested under the conditions described above. The results are reported in Table 1.

Example 8

A sample of catalyst IC1-97, tested under the same conditions as those of examples 1-5, but with a S/O ratio of 1.5, gave the results reported in Table 1. These results remained practically unaltered after 900 hours on stream.

TABLE 1

	Catalyst	S/O	Conv. of Ethylbenzene	Selectivity to Styrene	Mech. Strength
			Mol %	Mol %	
	IC1-90	2	69.26	93.06	fair
	IC1-95	2	75.30	93.37	good
	IC1-97	2	85.53	94.04	excellent
	IC1-99	2	77.40	94.01	excellent
25	IC1-100	2	65.35	94.68	excellent
	IC3-97a	2	73.42	94.58	fair
	IC3-97b	2	66.04	94.60	insufficient
	IC1-97	1.5	84.50	94.02	excellent

The above examples demonstrate that other conditions being the same (calcination temperature, nature of precursors and preparation procedure) the

presence of magnesium noticeably lowers both mechanical strength and conversion, while insignificantly affects selectivity (compare catalyst IC1-97, virtually magnesium-free, with IC3-97a, containing significant traces of MgO, and with IC3-97b, containing 1% of MgO).

- 5 For identical compositions, the higher the calcination temperature, the higher the mechanical strength of the catalyst (compare catalysts IC1-90, IC1-95, IC1-97, IC1-99 and IC1-100). When the calcination temperature exceeds 970°C, a considerable decrease of activity can be observed, the decrease being remarkable when the calcination temperature exceeds 990°C (compare
- 10 catalysts IC1-97, IC1-99 and IC1-100).

CLAIMS

1. A catalyst for the dehydrogenation of ethylbenzene to styrene, containing iron oxide, potassium oxide and calcium oxide, characterised in
5 that the magnesium content expressed as magnesium oxide is lower than 0.001%.
2. A catalyst according to claim 1 characterised in that it also contains cerium oxide and molybdenum oxide.
3. A catalyst according to claim 2, comprising: 50-95% Fe_2O_3 , 5-20%
10 K_2O , 0.2-14% CaO , 0.5-20% CeO_2 , 0.2-8 MoO_3 .
4. A catalyst according to claim 3, comprising: 60-85% Fe_2O_3 , 5-15% K_2O , 0.5-2% CaO , 5-15% CeO_2 , 0.5-2 MoO_3 .
5. A catalyst according to claim 4, comprising: 75-80% Fe_2O_3 , 8-12% K_2O , 0.7-1.4% CaO , 8-12% CeO_2 , 0.7-1.4 MoO_3 .
- 15 6. A catalyst according to claim 5, comprising: 78% Fe_2O_3 , 10% K_2O , 1% CaO , 10% CeO_2 , 1% MoO_3 .
7. A process for the preparation of the catalyst of any one of claims 1 - 6, comprising:
 - pre-mixing iron, calcium, potassium, cerium and molybdenum salts,
20 hydroxides or variously hydrated oxides;
 - adding a solution or a suspension of a binder-lubricating agent so as to obtain a paste;
 - extruding the paste in cylindrical particles of diameter and length ranging from 2 to 6 mm;
 - 25 - submitting said cylindrical particles to drying and calcinationcharacterised in that the catalyst contains less than 0.001% of magnesium, expressed as magnesium oxide.
8. A process according to claim 7, characterised in that the final

calcination of the catalyst is carried out in a temperature range from 950 to 990°C.

9. A process according to claim 8, characterised in that the final calcination is carried out in a temperature range from 960 to 980°C.

5 10. A process according to claim 9, characterised in that the final calcination is carried out in a temperature range from 965 to 975°C.

11. A process according to claim 10, characterised in that the final calcination is carried out at 970°C.

10 12. A process according to anyone of claims 6-11, characterised in that the final calcination time ranges from 30 min to 10 hours.

13. A process according to claim 12, characterised in that the final calcination time ranges from 1 hour to 4 hours.

14. A catalyst obtainable according to the process of any one of claims 7 – 13.

15 15. A process for the dehydrogenation of ethylbenzene to styrene which comprises passing a flow of ethylbenzene and water vapour through a bed of particles of the catalyst of any one of claims 1 – 6 and 14.

16. A process according to claim 15, characterised in that the water/ethylbenzene ratio is lower than 2.

20 17. A process according to claim 16, characterised in that the water/ethylbenzene ratio not higher than 1.5.

INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C5/333

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 467 046 A (SMITH JAMES L ET AL) 21 August 1984 (1984-08-21) cited in the application column 2, line 21 - line 26 column 3, line 19 - line 57 column 5, line 11 - line 14	1-17
X	EP 0 297 657 A (SHELL INT RESEARCH) 4 January 1989 (1989-01-04) examples 1,2	1,7-17
X	US 4 720 604 A (CHU CHIN-CHIUN) 19 January 1988 (1988-01-19) example 2	1
A	US 5 824 831 A (MATSUI JUNSHI ET AL) 20 October 1998 (1998-10-20) column 6, line 66 - column 7, line 4	1-17
	-/-	



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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 794 004 A (MONTECATINI TECNOLOGIE SRL) 10 September 1997 (1997-09-10) page 5, line 1 - line 15 -----</p>	1-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/03317

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4467046	A	21-08-1984	NONE	
EP 0297657	A	04-01-1989	FR 2617060 A1	30-12-1988
			AU 599813 B2	26-07-1990
			AU 1845688 A	05-01-1989
			BR 8803152 A	31-01-1989
			CA 1310952 C	01-12-1992
			CN 1032119 A ,B	05-04-1989
			DE 3872777 D1	20-08-1992
			DE 3872777 T2	25-02-1993
			EP 0297657 A1	04-01-1989
			ES 2042710 T3	16-12-1993
			FI 883072 A	30-12-1988
			GR 3005209 T3	24-05-1993
			JP 1027646 A	30-01-1989
			MX 173254 B	14-02-1994
			PL 273341 A1	20-03-1989
			SU 1836141 A3	23-08-1993
			US 4857498 A	15-08-1989
US 4720604	A	19-01-1988	NONE	
US 5824831	A	20-10-1998	CA 2181314 A1	17-01-1998
			JP 7178340 A	18-07-1995
EP 0794004	A	10-09-1997	IT MI960447 A1	08-09-1997
			AT 242660 T	15-06-2003
			AU 716285 B2	24-02-2000
			AU 1510397 A	11-09-1997
			BR 9701231 A	25-08-1998
			CA 2199218 A1	08-09-1997
			CN 1161882 A ,B	15-10-1997
			CZ 9700650 A3	17-09-1997
			DE 69722689 D1	17-07-2003
			EP 0794004 A1	10-09-1997
			HR 970129 A1	30-04-1998
			HU 9700554 A2	02-03-1998
			JP 10000359 A	06-01-1998
			NO 971062 A	09-09-1997
			PL 318846 A1	15-09-1997
			RU 2167711 C2	27-05-2001
			SK 30497 A3	10-09-1997
			TW 444003 B	01-07-2001
			US 6166280 A	26-12-2000

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